PATENT SPECIFICATION

DRAWINGS ATTACHED

Inventor: DAVID WADE RHYS

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1,150,356

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Int. Cl.: —C 22 c 5/00

COMPLETE SPECIFICATION

Coating Bodies of Oxidisable Elements and Alloys with Gold Alloys

We, INTERNATIONAL NICKEL LIMITED, a British Company of Thames House, Millbank, London, S.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The elements ruthenium, iridium, tungsten and molybdenum are strong but easily oxidised at elevated temperatures. The same applies to various alloys of these elements. In particular, when the surfaces of articles made of or coated with these metals or alloys are raised to temperatures of 900°C. or above in air volatile oxides readily form, and the surfaces lose weight at a rate which varies with the rate of air flow over them. This is particularly unfortunate because, for example, ruthenium and iridium have high strength above 900°C and are attractive to the glass industry since they are not attacked by some reactive glasses that corrode platinum.

If thin oxidation-resisting coatings can be applied to these elements or alloys, or to articles made from them, full use can be made of their desirable properties at elevated temperatures. Unfortunately oxidation-resistant metals which can be applied as coatings will readily diffuse into the body of the metal or alloy, with the result that the resistance to oxidation is rapidly lost.

According to the invention we provide an article for use at a given elevated temperature formed from a body protected by an oxidation-resistant coating, the body consisting essentially of iridium, ruthenium, molybdenum or tungsten, or consisting of one of these metals alloyed with gold, palladium, platinum, gold and palladium, or gold and platinum, with or without up to 5% of other metallic elements and being such that it would form volatile oxide at the given elevated temperature in the absence of an oxidation-resistant coating, and the oxidation-resistant coating being an alloy which will not diffuse, or which will diffuse only to a negligible extent, into the body at the given temperature, the composition of the body being at one end of a tie line or within a circle around one end of a tie line having a radius equal to the length on the axis of the ternary diagram on which the tie line is drawn corresponding to a 5% change in composition and the composition of the coating being at the other end of the tie line or within a circle around the other end of the line line also having a radius equal to the length on the axis of the ternary diagram corresponding to a 5% change in composition, the tie line being drawn on a ternary equilibrium diagram for the given temperature, one apex of which represents iridium, ruthenium, molybdenum or tungsten, a second apex of which represents gold, and the third apex of which represents palladium or platinum.

Articles of which the body contains iridium or ruthenium are valuable, and then the body may be composed of iridium or ruthenium, alloyed with palladium, platinum, or gold and platinum, and the coating consists of gold alloyed with platinum or palladium with or without iridium or ruthenium.

The invention is based on the discovery that if we prepare a ternary equilibrium diagram, one apex being iridium, ruthenium, molybdenum or tungsten, the second apex being gold and the third apex palladium or platinum, then a curve can be drawn as the boundary between single-phase and two-phase alloys. The position of this curve depends on the temperature. There may also be present on the diagram areas representing three-phase alloys, but for the purpose of the present invention these areas may be ignored. To ascertain the exact shape of each curve in any ternary system involves much detailed work, but the general form of the curve can be obtained fairly readily by standard metallographic techniques. In any two-phase alloy, the two phases will be those of two terminal solid solutions, and these will not diffuse into one another; all terminal solid solutions at the temperature in question lie on the boundary curve separating single-phase and two-phase alloys, and a line joining the points in the ternary diagram that represent the compositions of two terminal solid solutions which are in equilibrium with one another and which will not interdiffuse is called a tie line. In the invention, we make the body of the article from a composition which is at or within 5% of one end of a suitable tie line and which is that of a strong but oxidisable metal or alloy, and the oxidation-resistant coating from a composition which is at or within 5% of the other end of the same tie line and which is that of an oxidation-resistant alloy.

Ternary equilibrium diagrams may be extremely complicated, but for the purpose of describing the invention we are assuming that the equilibrium can be shown in terms of single- and two-phase alloys only. We ignore the fact that three-phase alloys may be present, and that there may be areas on the diagrams where a liquid phase is present. At the same time, clearly one cannot form the body or coating of an article from a composition which is liquid at the operating temperature at which one is to use the article, or from a composition having a solidus temperature below this operating temperature since such compositions will be mechanically weak. In some cases a circle drawn at 5% radius about the end of a tie-line may include within it compositions which are liquid or have too low a solidus temperature, and therefore obviously cannot be used as the body or the coating of an article according to the invention for one or other of these stated reasons.

The invention is concerned primarily with the protection of bodies formed from or containing a substantial proportion, that is at least 85%, of iridium, ruthenium, molybdenum or tungsten, alloyed with palladium, gold, or palladium and gold, but no platinum. However, the invention can be extended to bodies of ruthenium with palladium or platinum, which contains as little as 5% ruthenium, or to bodies of iridium with palladium or platinum which contain as little as 10% iridium. When we draw a ternary diagram for any one of iridium, ruthenium, molybdenum or tungsten together with gold and platinum, we find that the boundary curve is such that the tie-lines run generally from the platinum corner to the opposite side of the diagram. Since this means that only platinum-rich alloys can be protected with an alloy of gold and platinum, the technique of the invention is more frequently applicable to the use of gold and platinum. The bodies may also contain up to 5% in all of other incidental elements included to improve the properties of these metals; up to 0.5% in all of titanium or zirconium or both may be added to iridium to form an alloy, for example as described and claimed in our Specification No. 1016809 and up to 2.5% of ruthenium may be added to ruthenium, for example as described and claimed in our Specification No. 1032005:

Provided the quantity of other incidental elements added to the body is as low as 5%, the presence of the incidental elements can be ignored, and suitable compositions for body and oxidation-resistant coating calculated as before on a ternary diagram.

The invention will now be described with reference to Figures 1 to 10 of the accompanying drawings, each of which is a ternary equilibrium diagram. In each Figure, the boundary curve between single-phase and two-phase alloys is indicated by A, the plain area denoting two-phase alloys or three-phase alloys when present and the hatched area single-phase alloys.

Figure 1 represents the system Ru-Au-Pd at 1200°C. To find an appropriate alloy to protect a body of ruthenium or consisting predominantly of ruthenium is a fairly simple matter. In any two-phase alloy it is possible by, *inter-alia,* an electron probe micro-analyser to determine the compositions of the two phases in it, and these will be the compositions of two alloys which will not interdiffuse. Thus, considering Figure 1, an alloy containing for example 20% ruthenium, 20% gold and 60% palladium, and thus at the point M, is found by the electron probe to contain two phases, of composition 99% ruthenium, 1% palladium, and 73% palladium, 25% gold, 2% ruthenium respectively. An alloy of composition 99% ruthenium, 1% palladium lies at the point N, and an alloy of 73% palladium, 25% gold, 2% ruthenium

lies at the point P. A straight line Z joining N and P and passing through M is the tie line of the phases. A second alloy containing 20% ruthenium, 30% gold and 50% palladium (and therefore at M′) contains two phases, one of substantially 100% ruthenium at N′ and the other 62% palladium, 37% gold, 1% ruthenium at P′. Further alloys can be prepared and analysed, and the boundary curve A defined to any desired degree of accuracy; in this system at 1200°C, the boundary curve A is found to merge into the ruthenium axis at 22% ruthenium and into the palladium axis at 50% palladium.

The tie lines Z and Z′ indicate that a body of 99% ruthenium, 1% palladium can be protected by a coating of 73% palladium, 25% gold, 2% ruthenium, and that a body of substantially pure ruthenium can be protected by a coating of 62% pallidium, 37% gold, 1% ruthenium.

Provided that the general position of the boundary curve is known for any system at any temperature, it is not in fact absolutely necessary to determine the composition of more than one phase in the two-phase alloy in order to draw any tie line, since a straight line will invariably pass through the points representing the overall composition of the alloy itself and both phases. If one phase is ascertained, the second phase will therefore be of the composition at the point where the tie line intersects the boundary line.

Each of the remaining Figures 2 to 10 will now be described briefly; each is essentially similar to Figure 1 and may be obtained and interpreted in the same way.

Figure 2 shows the system Ir-Au-Pd at 1450°C. A body of 94 %iridium, 7% palladium may be protected by a coating of 63.5% palladium, 36% gold, 0.5% iridium, and a body of 91% iridium, 9% palladium may be protected by a coating of 71% palladium, 27% gold, 2% iridium, as shown by the tie lines Y and Y′.

Figure 3 shows the system Ir-Au-Pd at 1200°C. A body of substantially pure iridium may be protected by a coating of 79% palladium, 16% gold, 5% iridium, or by a coating of any other alloy on the boundary curve A containing less than 79% palladium and less than 5% iridium; a body of 98% iridium, 2% palladium may be protected by a coating of 80% palladium, 13% gold, 7% iridium, and a body of 88% iridium, 12% palladium may be protected by a coating of 79% palladium, 6% gold, 15% iridium, as shown by the tie lines X, X′ and X″.

Figure 4 shows the system Ru-Au-Pt at 1100°C. A body of 63% platinum, 37% ruthenium may be protected by a coating of 92% gold, 8% platinum, and a body of 86% platinum, 10% ruthenium, 4% gold may be protected by a coating of 73% gold, 27% platinum, as shown by the tie lines W and W′.

Figure 5 shows the system Ir-Au-Pt at 1200°C. A body of 90% platinum, 5% iridium, 5% gold may be protected by a coating of 71% gold, 29% platinum as shown by the tie line V.

Figure 6 shows the system Mo-Au-Pd at 1200°C. A body of substantially pure molybdenum may be protected by a coating of 44% palladium, 54% gold, 2% molybdenum, and a body of 97% molybdenum, 3% palladium may be protected by a coating of 76% palladium, 16% gold, 8% molybdenum, as shown by the tie lines U and U′.

Figure 7 shows the system Mo-Au-Pd at 1450°C. A body of 99% molybdenum, 1% palladium may be protected by a coating of 67% palladium, 30% gold, 3% molybdenum and a body of 97% molybdenum, 3% palladium may be protected by a coating of 76% palladium, 16% gold, 8% molydenum, as shown by the tie lines T and T′.

Figure 8 shows the system W-Au-Pd at 1200°C. A body of substantially pure tungsten may be protected in at least three ways as shown, by coatings of 75.5% palladium, 21.5% gold, 3% tungsten, or 65% palladium, 33% gold, 2% tungsten or 46% palladium, 52% gold, 2% tungsten. A body of 99% tungsten, 1% palladium may be protected by a coating of 79% palladium, 16% gold, 5% tungsten. These tie lines are shown, respectively, as S, S′, S″ and S‴.

Figure 9 shows the system W-Au-Pd at 1450°C. A body of substantially pure tungsten may be protected by a coating of 64.5% palladium, 43.5% gold, 3% tungsten, a body of 99% tungsten, 1% palladium may be protected by a coating of 72% palladium, 24% gold, 4% tungsten and a body of 98% tungsten, 2% palladium may be protected by a coating of 78.5% palladium, 16% gold, 5.5% tungsten. These tie lines are indicated by the reference numerals R, R′ and R″.

Figure 10 shows the system W-Au-Pt at 1100°C. A body of 84% platinum, 15% tungsten, 1% gold may be protected by a coating of 87% gold, 13% platinum, and a body of 69% platinum, 30% tungsten, 1% gold may be protected by a coating of 90% gold, 10% platinum, as shown by the tie lines Q and Q′.

If the body of an article according to the invention has a composition exactly on one end of a tie line, and the coating has a composition exactly on the other end of the tie line, then there will be no interdiffusion. In general, however, a certain tolerance is permissible, and broadly speaking a body having a composition such that it lies within a circle or part of a circle struck at a radius corresponding to a 5% change in composition on the axis from one end of a tie line can be used with a coating having a composition

such that it lies within a similar circle or part of a circle round the point forming the other end of the tie line, provided of course, that the composition is not liquid, or does not have a low solidus temperature, as stated above. Such part circles are shown, for example, as H and H' on tie line Y in Figure 2, and may be similarly drawn in all the other Figures. In most cases, the part circle includes within it the point where the tie line if extended would cut an axis of the ternary diagram, and thus a binary alloy will fall within the circle. Ideally the body and coating of an article should be formed from the exact compositions forming the ends of the tie lines, but in practice very good results will be often obtained using the binary alloy falling within the part circle, and there are definite advantages to be gained by doing this, as regards ease of production and cheapness.

Apart from Figures 4 and 10, which illustrate systems at 1100°C because the Pt-Au phase melts at 1200°C, all the remaining Figures show systems at 1200°C or 1450°C. While there is nothing in any way limiting about these temperatures, they have been chosen as representing typical temperatures at which articles according to the invention might operate in practice, many applications involving 1200°C or above. For example an iridium spinner for use in the production of glass fibre will run at 1200°C or higher, and turbine blades of molybdenum or tungsten may well operate at between 1200°C and 1450°C. From these Figures, the general direction of the tie lines can be seen. If the body of an article is to be of a certain composition, then the composition of a coating which will not diffuse into the body may be formed by determining and drawing an appropriate tie line. Once the compositions have been established, a suitable layer of the coating, which may be as little as 0.001 inch thick, is applied to the body.

In general the body of the article may be prepared by conventional techniques, but we prefer that the alloy for the coating be prepared initially by vacuum melting or powder metallurgical processes to avoid, or reduce the possibility of, gas being trapped within the alloy. The coating may be applied to the body in various ways depending on the shape or form of the body. If the body is a sheet or slab, then the coating may be applied in the form of sheet and bonded to the body by rolling; if the edges of a slab are to be coated as well, then the so-called "picture frame" technique may be used in which the slab is sandwiched between two flat sheets, with a strip of the coating alloy along the edges of the slab, air is exhausted from the interior of the assembly and the assembly is welded together, with subsequent rolling if necessary to the required thickness.

Articles in the form of coated wire may be prepared by forming the body as a cylindrical core, slipping the coating alloy in the form of a sleeve over the core, sealing the ends of the assembly and pumping out the air, and then swaging and hot-wire-drawing to the requisite diameter.

When the body is of complex shape, the coating may be applied by electrodeposition methods in which the various metals forming the alloy of the coating are applied independently in the correct proportions and then fused. If desired the body may be dipped into a bath of the molten alloy, or the alloy applied to it by metal spraying or plasma arc spraying. As a further possibility, the coating alloy may be applied by the flake powder technique described in our Patent Specification No. 952493.

WHAT WE CLAIM IS:—

1. An article for use at a given elevated temperature formed from a body protected by an oxidation-resistant coating, the body consisting essentially of iridium, ruthenium, molybdenum or tungsten, or consisting of one of these metals alloyed with gold, palladium, platinum, gold and palladium, or gold and platinum, with or without up to 5% of other metallic elements and being such that it would form volatile oxide at the given elevated temperature in the absence of an oxidation-resistant coating, and the oxidation-resistant coating being an alloy which will not diffuse, or which will diffuse only to a negligible extent, into the body at the given temperature, the composition of the body being at one end of a tie line or within a circle around one end of a tie line having a radius equal to the length on the axis of the ternary diagram on which the tie line is drawn corresponding to a 5% change in composition and the composition of the coating being at the other end of the tie line or within a circle around the other end of the tie line also having a radius equal to the length on the axis of the ternary diagram corresponding to a 5% change in composition, the tie line being drawn on a ternary equilibrium diagram for the given temperature, one apex of which represents iridium, ruthenium, molybdenum or tungsten, a second apex of which represents gold, and the third apex of which represents palladium or platinum.

2. An article according to claim 1, in which the body is composed of iridium or ruthenium, alloyed with palladium, platinum, or gold and platinum, and the coating consists of gold alloyed with platinum or palladium with or without iridium or ruthenium.

3. An article according to claim 1 in which the body contains at least 85% of iridium, ruthenium, molybdenum or tungsten alloyed with palladium, gold, or palladium and gold, but no platinum.

4. An article according to claim 1 in which the body contains iridium together with up to

0.5% in all of titanium or zirconium or both.

5. An article according to claim 1 in which the body contains ruthenium together with up to 2.5% of rhenium.

6. An article according to any one of the preceding claims in which the alloy forming the oxidation-resistant coating was prepared initially by vacuum melting or powder metallurgical processes.

7. An article according to claim 1, formed from a body and an oxidation-resistant coating, the compositions of which are at the ends of any of the tie-lines shown on the ternary diagrams forming Figures 1 to 10 of the accompanying drawings, or are within a circle around the ends of any of these tie lines having a radius equal to the length corresponding to a 5% change in composition on the axes of the ternary diagrams.

For the Applicants:
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52, Chancery Lane,
London, W.C.2.

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5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

FIG. 1

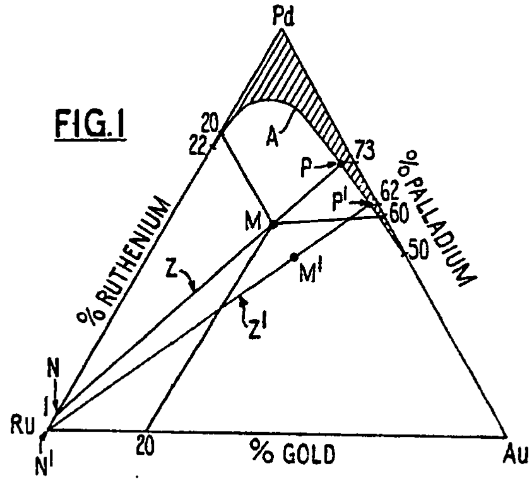


FIG. 2

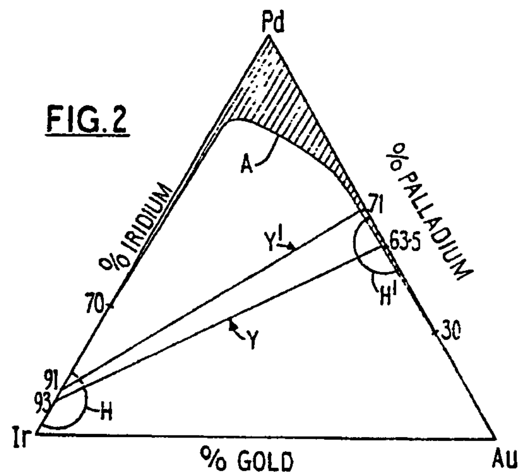


FIG.3

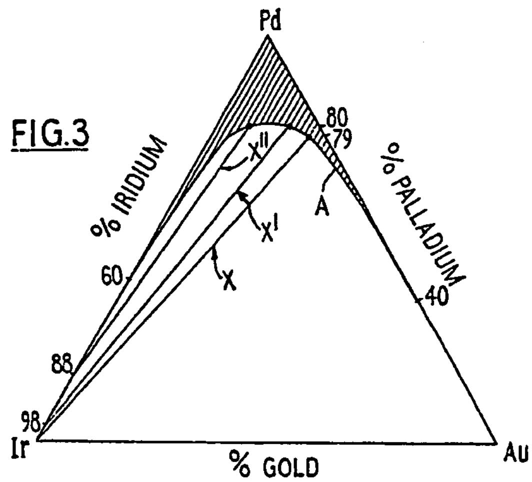
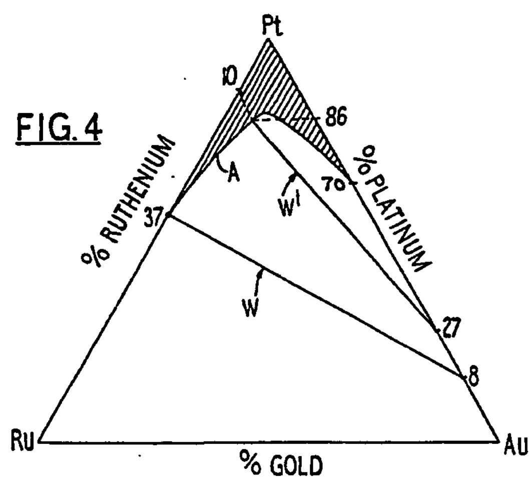

Pd
80
79
% IRIDIUM
X''
X'
A
% PALLADIUM
60
X
40
88
98
Ir
% GOLD
Au

FIG. 4


Pt
10
86
A
% RUTHENIUM
70
W'
% PLATINUM
37
W
27
8
Ru
% GOLD
Au

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Sheets 2 & 3

FIG.5

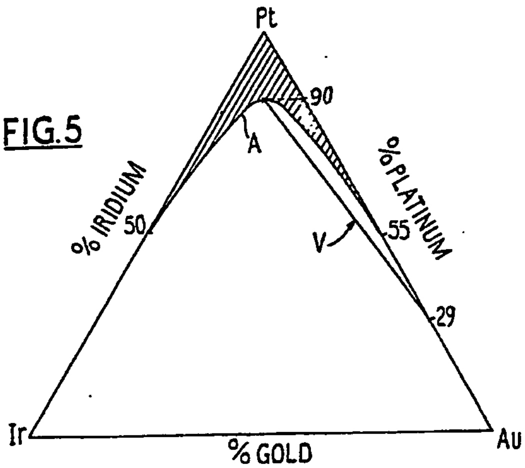
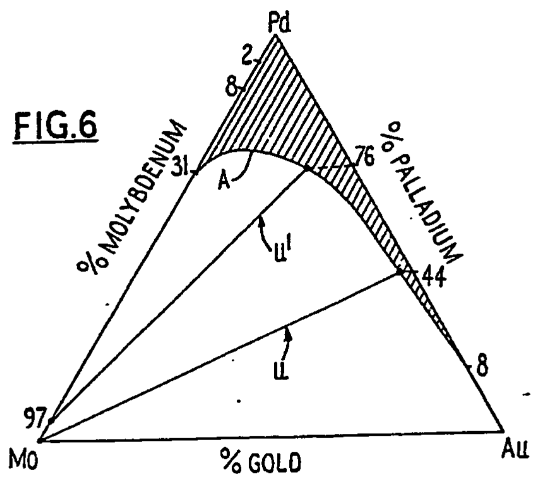


FIG.6



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Sheets 2 & 3

FIG.3

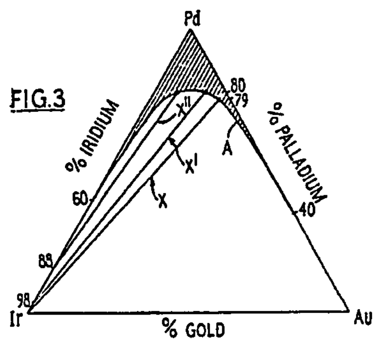


FIG.5

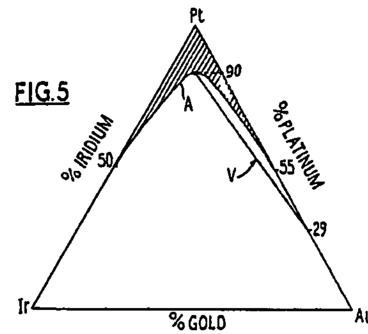


FIG.4

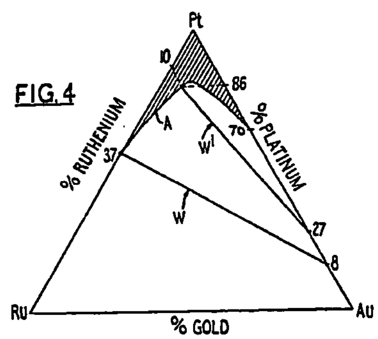


FIG.6

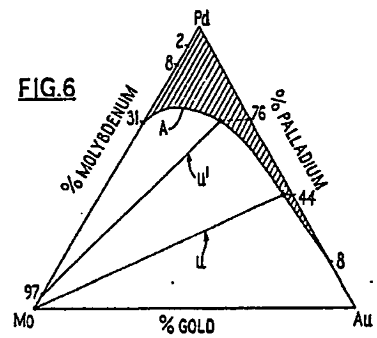


FIG.7

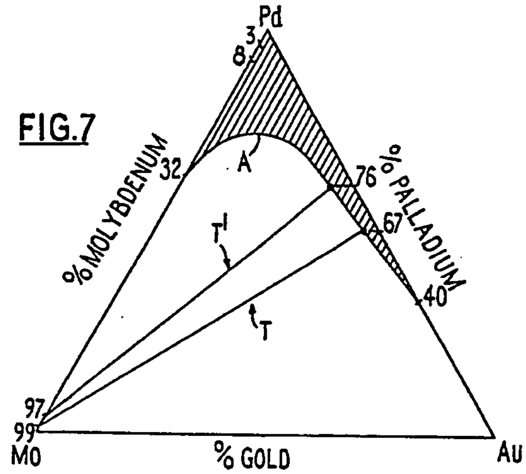
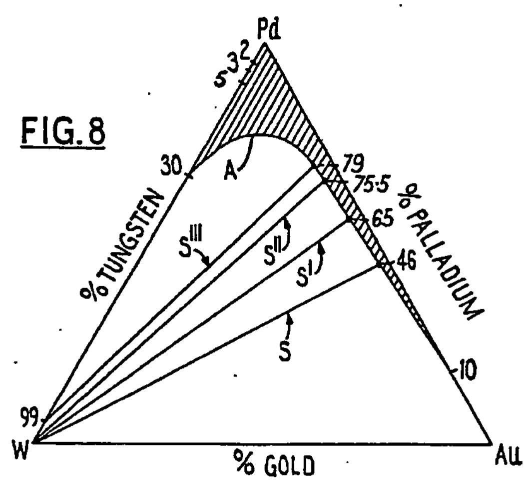

Pd
3
8
32
A
76
% PALLADIUM
67
40
% MOLYBDENUM
T'
T
97
99
MO
% GOLD
AU

FIG.8


Pd
5
3
2
30
A
79
75·5
% PALLADIUM
65
46
10
% TUNGSTEN
S'''
S''
S'
S
99
W
% GOLD
AU

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Sheets 4 & 5

FIG.9

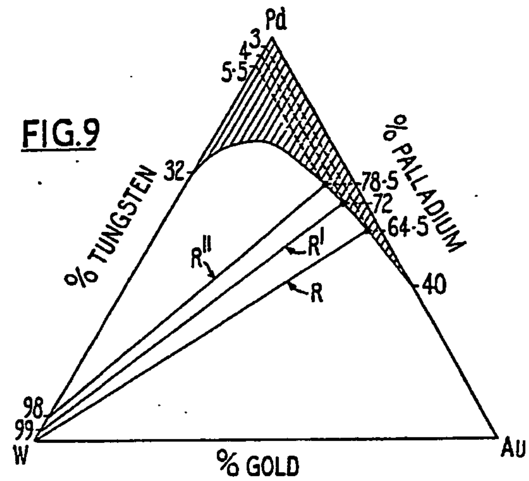
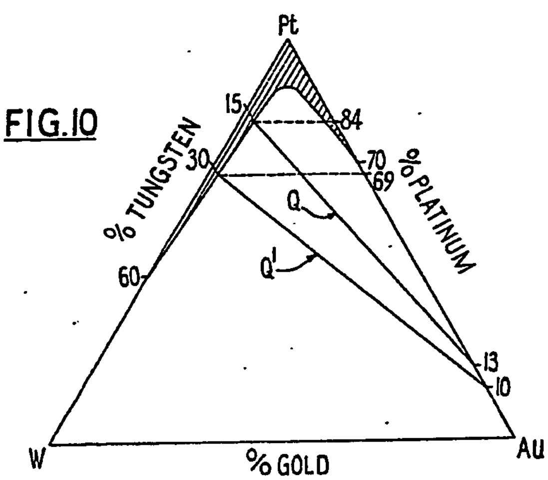


FIG.10



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Sheets 4 & 5

FIG.7

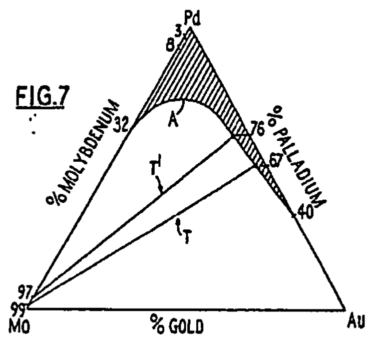

FIG.9

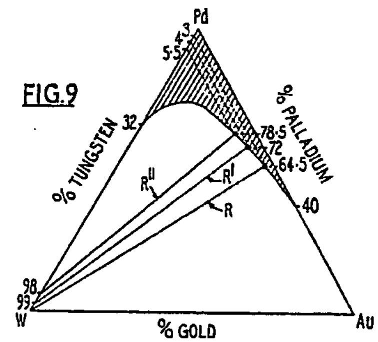

FIG.8

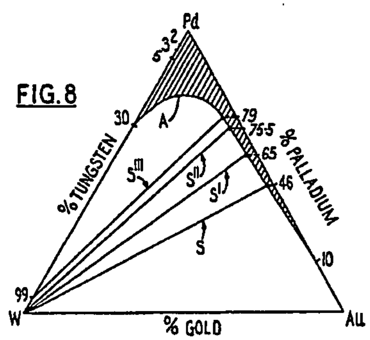

FIG.10